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ARTICLE

Polyaniline-Lemon Juice@Silica Nanocomposites an Efficient Catalyst for Synthesis of β -Amino Ketone

Pramod Kulkarni[✉] and Swati Kohinkar

ABSTRACT

The lemon juice anchored polyaniline nanoparticles were synthesized using aniline as a monomer and lemon juice as acid dopant with potassium persulfate as the oxidant. The synthesized nanoparticles were characterized by XRD, FESEM and EDX. The XRD pattern of polyaniline-lemon juice has been shown crystalline nature and the average size found to be 2.998 nm. The polyaniline-lemon juice nanoparticles were immobilized on column silica by grinding method. The polyaniline-lemon juice@silica nanocomposite were characterized by XRD and FESEM. The XRD pattern of polyaniline-lemon juice@silica nanocomposite has been shown amorphous nature. This study has explored the catalytic application of these nanocomposites in the synthesis of various β -amino ketones *via* a one-pot three-component Mannich reaction of aldehydes, ketones and aromatic amines. This method provides a novel and enhanced amendment of three-component Mannich reaction in terms of mild reaction conditions and clean reaction profiles, using a small quantity of catalyst and simple workup procedure.

KEYWORDS

Polyaniline, Multicomponent reaction, Mannich reaction, Lemon juice, Nanocomposite, Silica.

INTRODUCTION

Multicomponent reactions (MCRs) are convergent reactions, in which three or more starting materials are taken in one vessel and react to form a single product, where basically all or most of the reactants are put in the newly formed product. In an MCR, a product is assembled according to a cascade of elementary chemical reactions. The challenge is to conduct an MCR in such a way that the network of pre-equilibrated reaction channel into the main product and do not yield side products. The result is clearly dependent on the reaction conditions: solvent, temperature, catalyst, concentration, the kind of starting materials and functional groups [1,2].

The synthesis of bioactive secondary metabolites through the formation of grids of carbon-carbon bonds has captivated synthetic organic chemists for entire generations [3]. The Mannich reaction is one of the most powerful tools for carbon-carbon bond forming reaction [4]. It produces β -amino carbonyl compounds, which are key building blocks for synthesis of a wide variety of nitrogen-containing drugs and natural products [5]. β -Amino carbonyl compound have important as valuable

building blocks for the synthesis of bioactive molecule such as the antibiotics [6]. The Mannich reaction is useful for the synthesis of secondary and tertiary amine derivatives [7,8]. Numerous β -amino ketones and their analogues exhibit potent activity of great interest in medicinal chemistry, such as antidiabetic activities, antioxidant activity, anti-inflammatory, antibacterial, antiviral, antifungal, analgesic and anticancer activity [9]. The various methods have been reported for synthesis of β -amino carbonyl compound [10-19]. Some of the reported methods has shortcomings like long reaction time, use of hazardous solvents *e.g.* chloroform, dichloromethane *etc.* use of expensive catalyst, tedious workup procedure, low yield, product was purified by column chromatography. Hence there is scope to develop a new method for synthesis of β -amino ketone.

Synthesis of useful fine chemicals by various reactions exploiting heterogeneous catalysts has been a well-recognized opportunity for contemporary chemists. Heterogeneous catalyst has numerous diverse rewards over homogeneous systems such as recoverability, reusability, less contamination of metal ions in the products, better activity in some cases [20]. The use of polymer-supported catalysts offers several merits in preparation procedures. The polymer is typically very stable even in an oxidative atmosphere. Polyaniline is one of the polymers, which can be used as a matrix for catalysts [21] and also polyaniline supported metal oxide has been extensively used as solid acid catalysts for various organic transformations such as oxidation, dehydrogenation, condensation, Michael, Suzuki-Miyaura cross-coupling and esterification reactions [22].

Conventional doping of PANI with HCl is liable to dedoping, the evolution of HCl on evaporation may damage the device. Industrial production of PANI uses strong inorganic acids, liberation of destructive acidic waste in the water bodies, which have an unfavourable impact on the ecosystem. Lemon juice is eco-friendly and biocompatible acidic solution; it is a less inexpensive material for the synthesis of PANI. Lemon juice contains many weak organic acids, which assist the slow polymerization reaction and directional configuration of polyaniline chains [23,24]. Very few reports available in literature on synthesis of the PANI-lemon juice [23,25]. Here, we have prepared the PANI-lemon juice@SiO₂ as a novel nanocomposites using grindstone method and characterized by FTIR, XRD, FESEM and EDX. The synthesized nanocomposites is used as a catalyst in Mannich reaction.

EXPERIMENTAL

The chemical and reagent were obtained from commercially available source and used further purification. The XRD result was obtained using D8 advance diffractometer, Bruker AXS. The field emission scanning electron microscopy (FESEM)-energy dispersive spectroscopy (EDS) were recorded on FESEM -FEI Nova Nano SEM 450 and EDS on Bruker XFlash 6I30. The FESEM has the configuration, resolution 1.0 nm at 15 kv, 1.4 nm at 1 kV and 1.8 nm at 3 kV and 30 pa. The EDS configuration is excellent energy resolution 123 eV at MnK α and 45 eV at C K α . The element detection range from 4 Be to 95 Am. The melting points were measured in open capillary method and are uncorrected. IR spectra were

recorded on alpha T BRUKER model. ¹H NMR and ¹³C NMR spectra were recorded at ambient temperature on a BRUKER AVANCE DRX-500 MHz spectrophotometer using CDCl₃ or DMSO-*d*₆ as the solvent and TMS as an internal standard. The liquid chromatography mass spectrometer (LC-MS) was recorded on Bruker Impact HD with Impact II UHR-TOF Mass Spectrometer System, Dionex UHPLC Ultimate 3000 System. The ionization source used is positive ESI & APCI. The elemental analysis were recorded on Thermo Scientific (FLASH 2000) Elemental Analyzer. The purity of newly synthesized compound and the development of the reaction was monitored by thin layer chromatography (TLC) on Merck pre-coated silica gel 60 F₂₅₄ aluminium sheets, visualized by UV light.

Preparation of polyaniline lemon juice catalyst: Lemon juice was extracted from lemon purchased from the local market. About 3.425 mL of aniline and 10 mL of lemon juice was dissolved in 80 mL of water and after 30 min, a clear solution was obtained. Potassium persulphate (20 mL of 0.2 M) was added dropwise to this solution to initiate the polymerization of aniline. The colour of the solution changes from colourless to brown. The solution was cooled in refrigerator and solid was allowed to settle at the bottom of the solution. The solution was filtered and the precipitated was washed with water, ice-cold ethanol to get pure product. The product was dried in oven at 60 °C.

Preparation of silica polyaniline lemon juice catalyst: Polyaniline lemon juice nanocomposite (0.2 g) and column silica gel (1 g) was grounded in mortar and pestle for 20 min, a fine powder of polyaniline lemon juice@SiO₂ was obtained.

Selection of solvent: The optimum solvent for the synthesis of β -amino ketone, several solvents like ethanol, water, CHCl₃, DMSO, CH₃CN, toluene, solvent free conditions at moderate temperature were accomplished. The results are reported in Table-1. However, higher yield (85%) was obtained in ethanol as solvent. Hence the reaction was extended with substituted benzaldehyde and substituted aniline in ethanol as the reaction medium.

TABLE-1
OPTIMIZATION OF SOLVENT FOR ONE POT
THREE COMPONENTS MANNICH REACTIONS^a

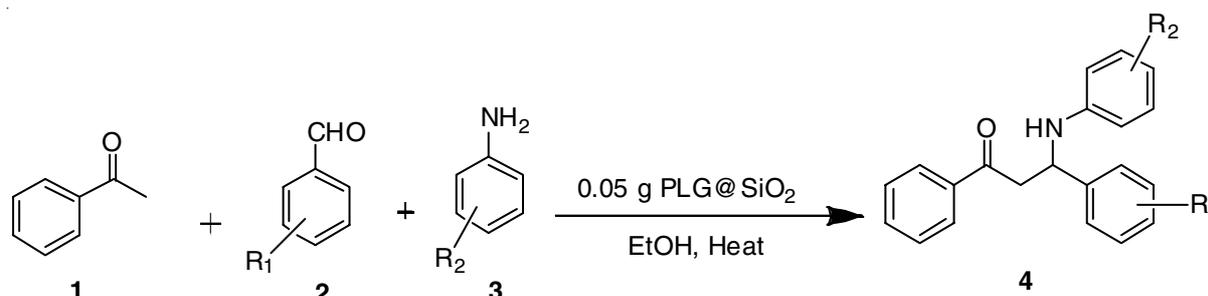
Entry	Solvent	Time (min)	Yield ^b (%)
1	EtOH	30	85
2	CHCl ₃	90	74
3	Toluene	60	65
4	Water	240	53
5	CH ₃ CN	180	70
6	DMSO	240	NR
7	Solvent free	80	82

^aReaction conditions: Acetophenone (5 mmol), benzaldehyde (5 mmol), & aniline (5 mmol), 0.05 g PLJ@SiO₂ in 10 mL solvent

^bIsolated yield after purification.

General procedure of the synthesis of β -amino ketone:

In a 25 mL round bottom flask, acetophenone (5 mmol), substituted benzaldehyde (5 mmol), substituted aniline (5 mmol) and silica doped polyaniline lemon juice catalyst (0.05 g) were dissolved in 10 mL ethanol. The mixture was refluxed, while stirred constantly. The progress of reaction was monitored by TLC. After completion of reaction, reaction mixture was cooled



Scheme-I: Polyaniline-lemon juice@SiO₂ catalyzed one-pot three component Mannich reaction for synthesis of β -amino ketones

at room temperature and then filtered the reaction mass to remove the catalyst and evaporate the filtrate to get crude product. The solid product was purified by recrystallization in the ethanol while the oily product was purified by column chromatography (**Scheme-I**).

Spectral data

1,3-Diphenyl-3-(phenylamino)propan-1-one (4a): Yield 85%, m.p. 167-169 °C. IR (KBr, ν_{\max} , cm⁻¹): 1262, 1345, 1630, 1684, 3393; ¹H NMR (500 MHz, CDCl₃, δ ppm): 3.44 (1H, d), 3.5 (1H, d), 4.5 (1H, s), 5.01 (1H, t), 6.5 δ (2H, d), 6.6 (1H, t), 7.09 (2H, t), 7.3 (1H, t), 7.4 (2H, m), 7.9 (1H, d); ¹³C NMR (125 MHz, δ ppm): 46.31, 54.82, 113.8, 117.8, 126.4, 127.35, 128.21, 128.70, 128.82, 129.10, 133.41, 136.72, 142.99, 146.99, 198.26. HRMS (M+H) (m/z): 302.15. Anal. calcd. (found) % for C₂₁H₁₉NO: C, 83.69 (83.61); H, 6.35 (6.30); N, 4.65 (4.57).

1-Phenyl-3-(phenylamino)-3-(3,4,5-trimethoxyphenyl)propan-1-one (4b): Yield 78%, m.p. 110-112 °C. IR (KBr, ν_{\max} , cm⁻¹): 1258, 1341, 1626, 1682, 3384; ¹H NMR (500 MHz, CDCl₃, δ ppm): 3.42 (1H, d), 3.47 (1H, d), 3.81 (3H, s), 3.85 (3H, s), 3.89 (3H, s), 4.54 (1H, s), 4.96-4.98 (1H, t), 6.54 (2H, s), 6.74-6.80 (m, 1H), 6.86-6.92 (2H, m), 7.18-7.25 (2H, m), 7.52-7.56 (2H, m), 7.60-7.64 (1H, m), 7.91-7.94 (2H, m); ¹³C NMR (125 MHz, δ ppm): 46.10, 55.23, 55.9, 55.7, 60.4, 102.5, 113.5, 120.3, 128.2, 128.9, 129.9, 133.2, 136.8, 137.5, 138.1, 147.6, 152.9, 198.6. HRMS (M+H) (m/z): 392.26. Anal. calcd. (found) % for C₂₄H₂₅NO₄: C, 73.64 (73.62); H, 6.44 (6.40); N, 3.58 (3.59).

3-(2,4-Dimethoxyphenyl)-1-phenyl-3-(phenylamino)propan-1-one (4c): Yield 73%, m.p. 115-118 °C. IR (KBr, ν_{\max} , cm⁻¹): 1240, 1346, 1622, 1678, 3374; ¹H NMR (500 MHz, CDCl₃, δ ppm): 3.35 (1H, d), 3.43 (1H, d), 3.83(3H, s), 3.87 (3H, s), 4.61 (1H, s), 4.98-5.01 (1H, t), 6.45-6.46 (1H, dd, J = 1.2 Hz, 8.5 Hz), 6.68-6.73 (1H, d, J = 1.2 Hz), 6.79-6.82 (1H, m), 6.86-6.89 (1H, m), 7.03-7.08 (1H, d, J = 8.5 Hz), 7.28-7.30 (2H, m), 7.52-7.55 (2H, m), 7.64-7.67 (m, 2H), 7.87-7.90 (2H, m); ¹³C NMR (125 MHz, δ ppm): 47.12, 55.8, 56.3, 60.8, 102.5, 100.3, 109.8, 113.7, 120.2, 121.3, 128.3, 128.9, 129.3, 129.6, 129.9, 133.4, 136.2, 157.3, 159.8, 198.9. HRMS (M+H) (m/z): 361.36. Anal. calcd. (found) % for C₂₃H₂₃NO₃: C, 76.43 (76.32); H, 6.41 (6.34); N, 3.88 (3.73).

3-(2-Bromophenyl)-1-phenyl-3-(phenylamino)propan-1-one (4d): Yield 70%, m.p. 153-155 °C. IR (KBr, ν_{\max} , cm⁻¹): 1260, 1345, 1623, 1686, 3376; ¹H NMR (500 MHz, CDCl₃, δ ppm): 3.39 (1H, d), 3.45 (1H, d), 4.57 (1H, s), 4.91-4.94 (1H, t), 6.71-6.74(m, 1H), 6.82-6.85 (2H, m), 7.10-7.13 (1H, m),

7.19-7.22 (1H, m), 7.29-7.33 (2H, m), 7.38-7.41 (1H, m), 7.51-7.53 (2H, m), 7.58-7.60 (1H, m), 7.66-7.69 (1H, m), 7.89-7.92 (2H, m); ¹³C NMR (125 MHz, δ ppm): 46.8, 61.1, 113.9, 120.6, 122.2, 127.3, 128.4, 128.6, 128.9, 129.2, 129.4, 132.3, 133.6, 136.8, 145.4, 147.2, 198.2. HRMS (M+H) (m/z): 381.34. Anal. calcd. (found) % for C₂₁H₁₈NOBr: C, 66.33 (66.32); H, 4.77 (4.42); N, 3.68 (3.45).

3-(2-Chlorophenyl)-1-phenyl-3-(phenylamino)propan-1-one (4e): Yield 75%, m.p. 137-139 °C. IR (KBr, ν_{\max} , cm⁻¹): 1262, 1341, 1626, 1688, 3378; ¹H NMR (500 MHz, CDCl₃, δ ppm): 3.36 (1H, d), 3.43 (1H, d), 4.52 (1H, s), 4.89-4.91 (1H, t), 6.67-6.69(m, 1H), 6.78-6.80 (2H, m), 7.06-7.09 (1H, m), 7.15-7.18 (1H, m), 7.25-7.28 (2H, m), 7.33-7.36 (1H, m), 7.46-7.49 (2H, m), 7.54-7.56 (1H, m), 7.62-7.65 (1H, m), 7.87-7.91 (2H, m); ¹³C NMR (125 MHz, δ ppm): 46.4, 60.9, 113.2, 120.1, 121.9, 126.8, 128.1, 128.7, 129.1, 129.5, 129.9, 132.1, 133.7, 136.4, 145.7, 146.9, 198.4. HRMS (M+H) (m/z): 336.45. Anal. calcd. (found) % for C₂₁H₁₈NOCl: C, 75.11 (75.08); H, 5.40 (5.33); N, 4.17 (4.12).

3-(4-(Dimethylamino)phenyl)-1-phenyl-3-(phenylamino)propan-1-one (4f): Yield 74%, m.p. 200-202 °C. IR (KBr, ν_{\max} , cm⁻¹): 1267, 1346, 1418, 1630, 1681, 3386; ¹H NMR (500 MHz, CDCl₃, δ ppm): 3.11 (6H, s), 3.24 (1H, d), 3.36 (1H, d), 4.48 (1H, s), 4.86-4.88 (1H, t), 6.58-6.61 (2H, d, J = 8.6 Hz), 6.71-6.73 (1H, m), 6.84-6.87 (2H, m), 7.11-7.14 (2H, d, J = 8.6 Hz), 7.21-7.24 (2H, m), 7.54-7.56 (2H, m), 7.62-7.65 (1H, m), 7.87-7.91 (2H, m); ¹³C NMR (125 MHz, δ ppm): 41.7, 46.2, 60.1, 112.4, 113.8, 120.4, 128.3, 128.8, 129.1, 129.7, 130.4, 133.8, 136.9, 147.6, 149.9, 197.8. HRMS (M+H) (m/z): 345.12. Anal. calcd. (found) % for C₂₃H₂₄N₂O: C, 80.20 (80.12); H, 7.02 (7.05); N, 8.13 (8.09).

3-(3-Nitrophenyl)-1-phenyl-3-(phenylamino)propan-1-one (4g): Yield 84%, m.p. 133-134 °C. IR (KBr, ν_{\max} , cm⁻¹): 1262, 1349, 1412, 1510, 1624, 1690, 3391; ¹H NMR (500 MHz, CDCl₃, δ ppm): 3.38 (1H, d), 3.52 (1H, d), 4.53 (1H, s), 4.97-5.01 (1H, t), 6.71-6.74 (1H, m), 6.86-6.89 (2H, m), 7.29-7.33 (2H, m), 7.56-7.59 (2H, m), 7.64-7.67 (1H, m), 7.71-7.74 (1H, m), 7.79-7.82(1H, m), 7.96-7.99 (2H, m), 8.05-8.08 (1H, m), 8.16-8.19 (1H, m); ¹³C NMR (125 MHz, δ ppm): 47.4, 61.3, 113.9, 120.3, 120.7, 122.2, 128.5, 128.9, 129.2, 129.6, 133.2, 133.5, 137.1, 144.3, 147.3, 147.7, 198.5. HRMS (M+H) (m/z): 347.18. Anal. calcd. (found) % for C₂₁H₁₈N₂O₃: C, 72.82 (72.78); H, 5.24 (5.20); N, 8.09 (8.08).

3-((4-Hydroxyphenyl)amino)-1,3-diphenylpropan-1-one (4h): Yield 68%, m.p. 171-173 °C. IR (KBr, ν_{\max} , cm⁻¹): 1257, 1338, 1619, 1678, 3294, 3372; ¹H NMR (500 MHz,

CDCl₃, δ ppm): 3.29 (1H, d), 3.40 (1H, d), 4.53 (1H, s), 4.90-4.93 (1H, t), 6.69-6.72 (2H, d, $J = 8.3$ Hz), 6.78-6.80 (2H, d, $J = 8.3$ Hz), 7.30-7.33 (1H, m), 7.36-7.39 (2H, m), 7.42-7.44 (2H, m), 7.49-7.53 (2H, m), 7.59-7.63 (1H, m), 7.86-7.90 (2H, m), 10.97 (1H, s, OH); ¹³C NMR (125 MHz, δ ppm): 45.9, 59.9, 116.4, 116.9, 126.4, 127.0, 128.4, 128.7, 128.9, 133.4, 136.8, 140.1, 140.9, 147.0, 197.3. HRMS (M+H) (m/z): 318.08. Anal. calcd. (found) % for C₂₁H₁₉NO₂: C, 79.47 (79.42); H, 6.03 (5.99); N, 4.41 (4.40).

3-(Ethyl(phenyl)amino)-1,3-diphenylpropan-1-one (4i): Yield 72%, m.p. 108-111 °C. IR (KBr, ν_{\max} , cm⁻¹): 1261, 1338, 1410, 1623, 1672; ¹H NMR (500 MHz, CDCl₃, δ ppm): 1.12-1.16 (3H, t, $J = 7.4$ Hz), 2.9 (1H, d), 3.13 (1H, d), 3.32-3.36 (2H, q, $J = 7.4$ Hz), 4.78-4.80 (1H, t), 6.72-6.75 (1H, d), 6.93-6.96 (2H, m), 7.22-6.24 (2H, m), 7.29-7.30 (1H, m), 7.34-7.36 (2H, m), 7.43-7.45 (2H, m), 7.51-7.53 (2H, m), 7.64-7.66 (1H, m), 7.96-7.98 (2H, m); ¹³C NMR (125 MHz, δ ppm): 15.5, 43.9, 46.8, 62.2, 111.4, 121.5, 127.1, 127.8, 128.3, 128.6, 128.8, 129.4, 133.3, 136.5, 141.9, 149.7, 197.2. HRMS (M+H) (m/z): 330.23. Anal. calcd. (found) % for C₂₃H₂₃NO: C, 83.85 (83.80); H, 7.04 (7.02); N, 4.25 (4.19).

3-(Naphthalen-1-ylamino)-1,3-diphenylpropan-1-one (4j): Yield 74%, m.p. 144-147 °C. IR (KBr, ν_{\max} , cm⁻¹): 1253, 1322, 1407, 1520, 1634, 1692, 3389; ¹H NMR (500 MHz, CDCl₃, δ ppm): 3.03 (1H, d), 3.25 (1H, d), 4.74 (1H, s), 4.64-4.67 (1H, t), 6.97-6.99 (1H, m), 7.24-7.26 (1H, m), 7.30-7.33 (1H, m), 7.36-7.38 (1H, m), 7.42-7.45 (2H, m), 7.50-7.52 (3H, m), 7.56-7.58 (1H, m), 7.60-7.62 (1H, m), 7.65-7.67 (1H, m), 7.96-7.99 (2H, m), 8.03-8.05 (1H, m), 8.10-8.13 (1H, m); ¹³C NMR (125 MHz, δ ppm): 47.1, 61.9, 109.5, 119.1, 124.8, 125.1, 125.9, 126.6, 127.9, 128.4, 128.6, 128.9, 133.4, 134.7, 136.3, 140.2, 147.8, 197.6. HRMS (M+H) (m/z): 352.19. Anal. calcd. (found) % for C₂₅H₂₁NO: C, 85.44 (85.39); H, 6.02 (6.01); N, 3.99 (3.94).

3-((4-Chlorophenyl)amino)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (4k): Yield 81%, m.p. 160-162 °C. IR (KBr, ν_{\max} , cm⁻¹): 1246, 1316, 1417, 1528, 1629, 1681, 3378; ¹H NMR (500 MHz, CDCl₃, δ ppm): 3.11 (1H, d), 3.32 (1H, d), 3.89 (3H, s, OCH₃), 4.67 (1H, s), 4.89-4.92 (1H, t), 6.49-6.52 (2H, d, $J = 8.6$ Hz), 6.89-6.93 (2H, d, $J = 8.6$ Hz), 7.13-7.16 (2H, d, $J = 8.1$ Hz), 7.30-7.33 (2H, d, $J = 8.1$ Hz), 7.48-7.51 (2H, m), 7.57-7.60 (2H, m), 7.93-7.96 (2H, m); ¹³C NMR (125 MHz, δ): 46.2, 55.8, 60.3, 113.9, 115.2, 126.3, 126.9, 128.3, 128.9, 130.1, 132.7, 133.3, 137.4, 145.9, 157.9, 197.1. HRMS (M+H) (m/z): 367.34. Anal. calcd. (found) % for C₂₂H₂₀NO₂Cl: C, 72.22 (72.26); H, 5.50 (5.45); N, 3.83 (3.78).

3-(4-Chlorophenyl)-3-((4-methoxyphenyl)amino)-1-phenylpropan-1-one (4l): Yield 88%, m.p. 104-106 °C. IR (KBr, ν_{\max} , cm⁻¹): 1243, 1313, 1410, 1518, 1624, 1682, 3371; ¹H NMR (500 MHz, CDCl₃, δ ppm): 3.15 (1H, d), 3.29 (1H, d), 3.87 (3H, s, OCH₃), 4.61 (1H, s), 4.85-4.87 (1H, t), 6.56-6.59 (2H, d, $J = 8.8$ Hz), 6.94-6.96 (2H, d, $J = 8.8$ Hz), 7.35-7.37 (2H, d, $J = 8.3$ Hz), 7.43-7.45 (2H, d, $J = 8.3$ Hz), 7.50-7.53 (2H, m), 7.59-7.62 (2H, m), 7.94-7.97 (2H, m); ¹³C NMR (125 MHz, δ ppm): 46.6, 55.2, 60.1, 113.4, 115.6, 126.7, 127.2, 128.5, 129.1, 130.3, 132.2, 133.8, 137.9, 146.2, 157.2, 197.8. HRMS (M+H) (m/z): 367.24. Anal. calcd. (found) % for C₂₂H₂₀NO₂Cl: C, 72.22 (72.16); H, 5.50 (5.47); N, 3.83 (3.80).

3-(4-Nitrophenyl)-3-((3-nitrophenyl)amino)-1-phenylpropan-1-one (4m): Yield 64%, m.p. 130-132 °C. IR (KBr, ν_{\max} , cm⁻¹): 1237, 1343, 1420, 1428, 1543, 1637, 1690, 3388; ¹H NMR (500 MHz, CDCl₃, δ ppm): 3.35 (1H, d), 3.49 (1H, d), 4.56 (1H, s), 4.94-4.97 (1H, t), 7.18-7.20 (1H, m), 7.47-7.49 (1H, m), 7.52-7.55 (2H, m), 7.58-7.60 (1H, dd, $J = 1.4$ Hz, 1.2 Hz), 7.61-7.63 (2H, d, $J = 8.4$ Hz), 7.65-7.67 (1H, m), 7.71-7.73 (1H, m), 7.98-8.00 (1H, m), 8.24-8.26 (2H, d, $J = 8.4$ Hz); ¹³C NMR (125 MHz, δ ppm): 47.8, 60.9, 105.1, 112.9, 119.9, 122.8, 123.6, 128.3, 128.7, 130.7, 133.8, 136.2, 145.7, 146.6, 148.1, 149.1, 198.2. HRMS (M+H) (m/z): 392.45. Anal. calcd. (found) % for C₂₁H₁₇N₃O₅: C, 64.45 (64.40); H, 4.38 (4.40); N, 10.74 (10.70).

1,3-Diphenyl-3-(pyridine-2-ylamino)propan-1-one (4n): Yield 73%, m.p. 116-118 °C. IR (KBr, ν_{\max} , cm⁻¹): 1253, 1332, 1454, 1609, 1686, 3370; ¹H NMR (500 MHz, CDCl₃, δ ppm): 3.45-3.53 (2H, d, $J = 6.8$ Hz), 5.10-5.14 (1H, br s), 5.26-5.33 (1H, t, $J = 6.8$ Hz), 6.36-6.45 (2H, m), 7.05-7.25 (5H, m), 7.38-7.44 (4H, m), 7.49-7.54 (2H, m), 7.81-7.86 (1H, m); ¹³C NMR (125 MHz, CDCl₃, δ ppm): 45.5, 71.6, 107.9, 113.2, 127.3, 128.3, 128.8, 129.6, 132.4, 133.7, 136.1, 137.6, 141.0, 147.2, 156.1, 197.4. HRMS (M+H) (m/z): 303.19. Anal. calcd. (found) % for C₂₁H₁₈N₂O: C, 79.44 (79.46); H, 6.00 (5.97); N 9.26 (9.18).

RESULTS AND DISCUSSION

A novel polyaniline containing dual acid components lemon juice and column silica gel was prepared. Firstly, PANI containing lemon juice as acid component was prepared by aqueous polymerization using potassium persulphate as an oxidant. In the next step, PANI containing lemon juice nanoparticle was anchored on column silica gel using grindstone method. A PANI-lemon juice and PANI-lemon juice@SiO₂ were characterized by XRD and FESEM techniques. In order to determine the crystallite size and phase composition of the prepared nanoparticles, XRD analysis (Siemens D5000 diffractometer) using CuK α radiation at 2 θ angle from 10° to 60°. The peaks were obtained at 18.81° (1 1 1), 20.15° (2 0 0), 23.68° (2 2 0), 26.06° (3 1 1) and 28.96° (2 2 2). The mean crystallite size of the nanoparticles was calculated using Scherrer's equation:

$$D = \frac{k(\lambda)}{\beta(\cos\theta)}$$

where D is the average size (nm), k is a constant equal to 0.89, λ is the X-ray wavelength equal to 0.154056 nm, β is the full width at half maximum intensity, θ is the half diffraction angle.

Generally, crystalline domain sizes decrease with increasing line broadening of the peaks. The average size of crystallites determined from the XRD pattern for PANI-lemon juice was found to be 2.998 nm. The XRD pattern of PANI-lemon juice-SiO₂ nano composite showed the amorphous nature. The XRD pattern of PANI-lemon juice and PANI-lemon juice-SiO₂ are shown in Figs. 1 and 2, respectively. The FESEM images of polyaniline-lemon juice is shown in Fig. 3. The flower like morphology of polyaniline-lemon juice was observed in FESEM images.

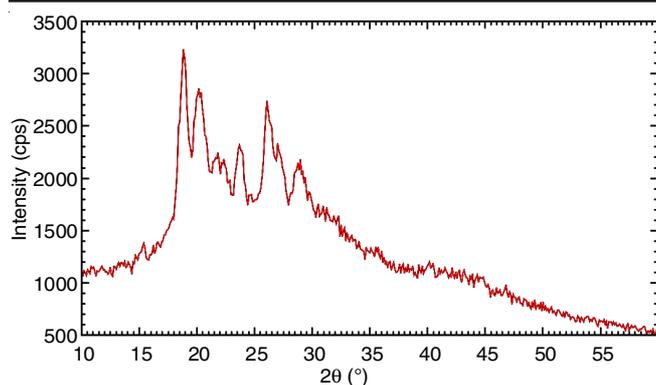


Fig. 1. XRD of polyaniline-lemon juice

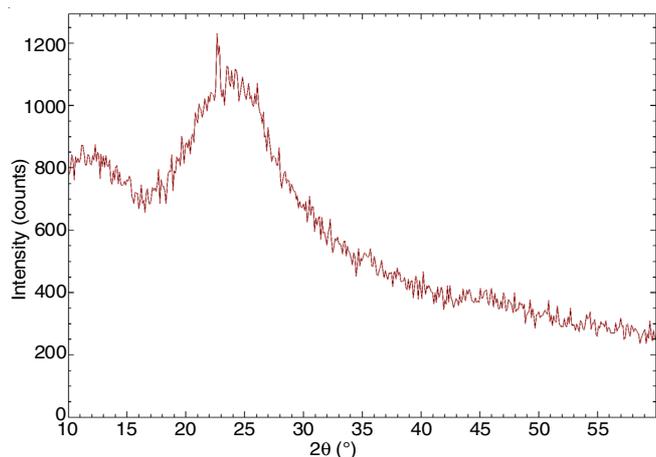


Fig. 2. XRD of polyaniline-lemon juice@silica

Chemistry: The two prepared catalysts were utilized for the one pot three component Mannich reactions between aromatic ketone, substituted benzaldehyde and substituted aniline. A model reaction between acetophenone, benzaldehyde and aniline was selected to study the efficiency of both

catalysts. Initially, about 0.1 g PANI-lemon juice was used as a catalyst for model reaction. The model reaction was carried in 10 mL ethanol under stirring with heating condition. It was observed that the reaction proceeded very slowly and isolation of product requires very tedious process.

Another new catalyst *viz.* PANI-lemon juice anchored on column silica gel results in the improvement of reaction rates, increasing the yield of the product and easy work-up procedure. Under experimental conditions, the model reaction was carried using 5 mmol of acetophenone, 5 mmol of benzaldehyde and 5 mmol of aniline using 0.05 mg PANI-Lemon juice@SiO₂ in 10 mL ethanol at moderate temperature. The progress of the reaction was monitored by TLC using ethyl acetate:petroleum ether (2:8). After completion of the reaction, filtered the reaction mixture to remove catalyst. The filtrate was evaporated to get crude β -amino ketone and further products were purified by recrystallization from ethanol. The products were characterized by ¹H NMR, ¹³C NMR and HRMS to confirm the structure of compounds.

The FT-IR spectrum of all the isolated compounds show the characteristic absorption frequencies in the range 3393-3370 cm⁻¹ for *sec.* NH, 3054-3040 cm⁻¹ for arom. CH *str.*, 1698-1670 cm⁻¹ for carbonyl *str.* and 1592-1568 cm⁻¹ for C=N *str.* are observed. In the ¹H NMR spectrum of compound **4a**, a signal at δ 3.44-3.5 ppm is multiplet due to methylene protons and signal at δ 5.01 ppm due to methyne protons which gives triplet because it couple with methylene proton. Fifteen aromatic protons appear in the range of 6.5-7.9 ppm. In ¹³C NMR, ¹³C resonance at δ 46.31 ppm due to the presence of a CH₂ carbon atom attached to carbonyl carbon and δ 54.82 ppm is due to CH carbon attached to nitrogen atom and aromatic ring. The carbon resonances observed at 113.8, 117.8, 126.4, 127.35, 128.21, 128.70, 128.82, 129.10, 133.41, 136.72, 142.99, 146.99 are due to aromatic carbons. Similarly, ¹³C resonance at 198.26 ppm corresponds to the carbonyl carbon.

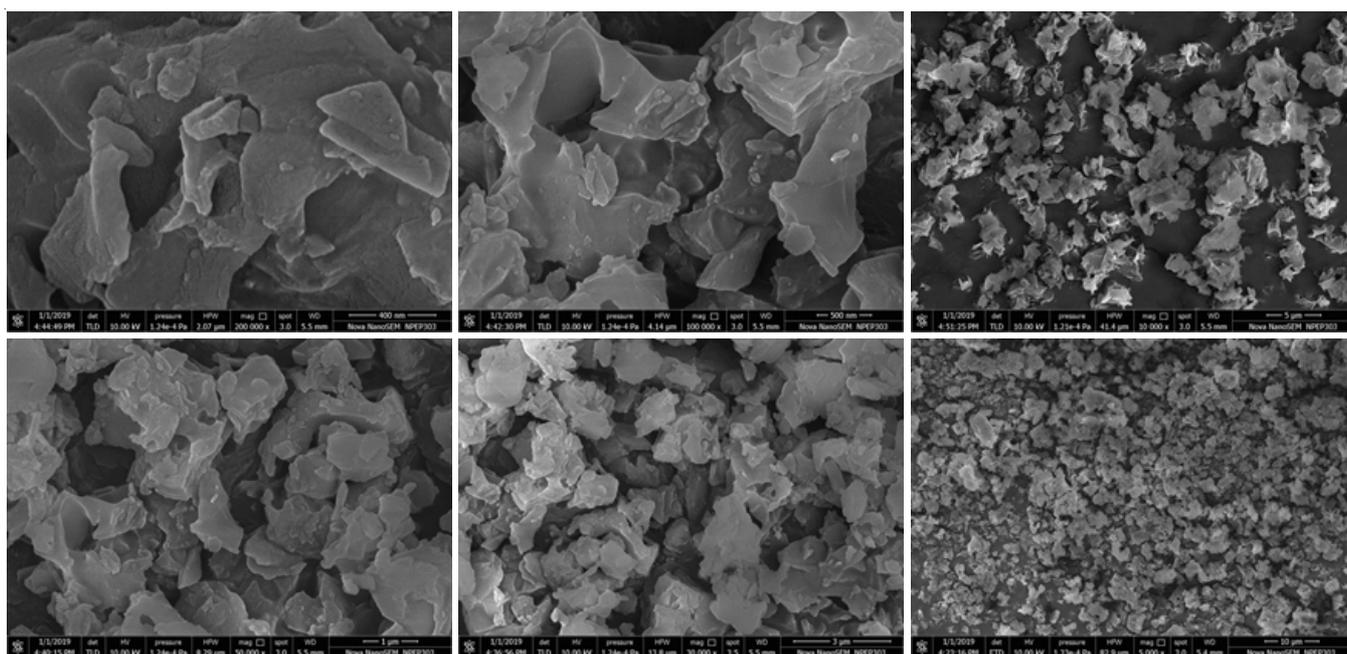
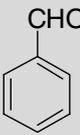
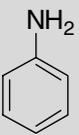
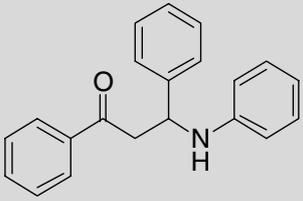
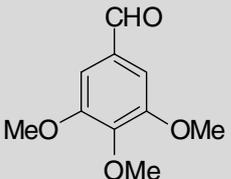
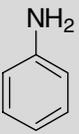
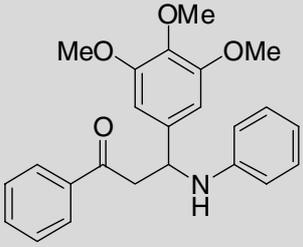
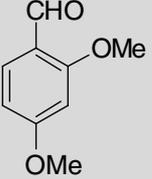
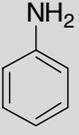
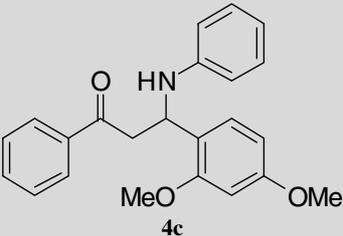
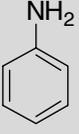
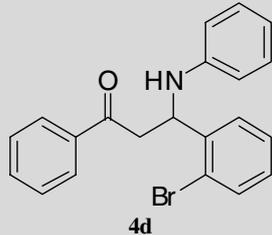
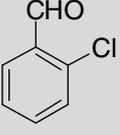
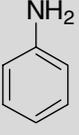
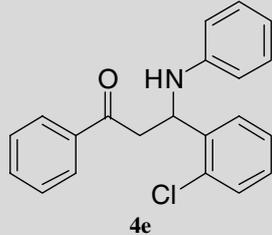
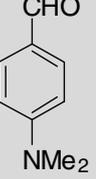
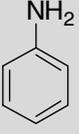
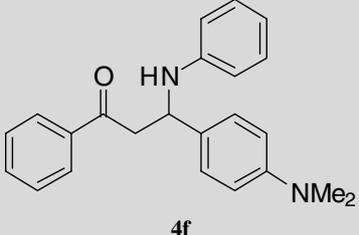
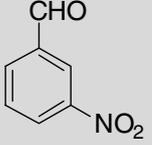
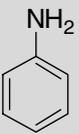
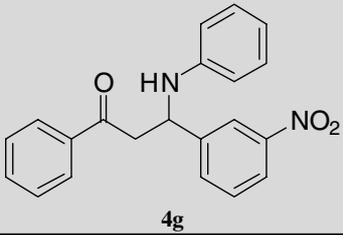
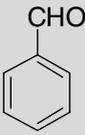
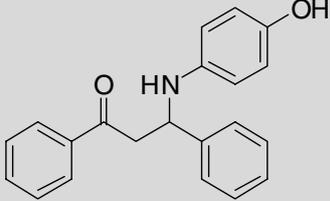
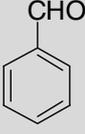
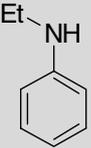
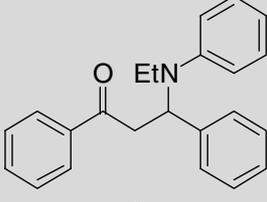
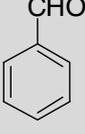
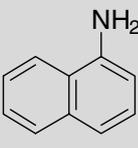
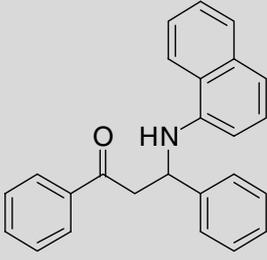
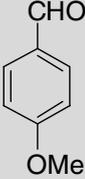
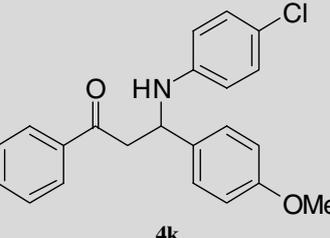
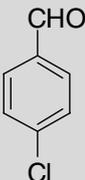
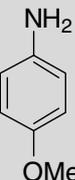
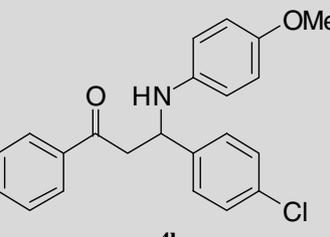
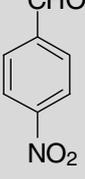
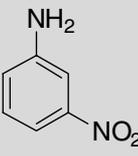
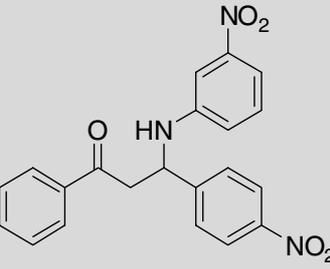
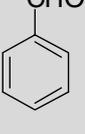
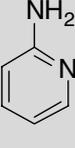
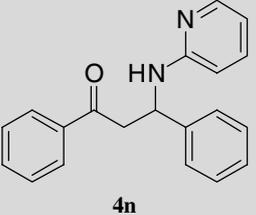


Fig. 3. FESEM images of polyaniline-lemon juice

TABLE-2
 POLYANILINE-LEMON JUICE@SILICA CATALYZED ONE POT THREE COMPONENT MANNICH
 REACTION OF KETONE, ALDEHYDE & ANILINE TO AFFORD β -AMINO KETONE^a

Entry	Aldehyde	Amines	Product (4)	Time (min)
1			 4a	30
2			 4b	70
3			 4c	85
4			 4d	120
5			 4e	100
6			 4f	90
7			 4g	30

8				130
9				160
10				80
11				50
12				40
13				50
14				100

^aReaction condition: Acetophenone (5 mmol), benzaldehyde (5 mmol), & substituted aniline (5 mmol), 0.05 g silica polyaniline lemon juice in 10 mL ethanol. ^bAll yield of product are pure after recrystallize & column chromatography.

The nature and position of functional group on the phenyl ring affected the reaction time and yield of the product. The results indicated that aryl aldehyde containing functional group such as -Br, -NO₂, -OH reacted with acetophenone and aniline to afford the high yield of product (Table-2).

Conclusion

Two polyaniline based nanocomposites *viz.* polyaniline-lemon juice nanocomposites and polyaniline-lemon juice@silica using grindstone method were prepared and characterized by XRD and FESEM, EDX. The XRD pattern of polyaniline-lemon juice has shown the crystalline nature while polyaniline-lemon juice@silica exhibited the amorphous nature. The catalytic activity of both nanocomposites was studied in one-pot three component Mannich reaction for synthesis of β-amino ketone. The better yield of the product was observed in solvent than solvent free conditions and ethanol was found to be an ideal solvent for this reaction. The method offers several merits, which includes low catalyst loading, operational simplicity, high yield, use of non-hazardous chemical and eco-friendly method. The catalytic activity of polyaniline-lemon juice@silica is catalytically more active than polyaniline-lemon juice.

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